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A Green's function approach to estimate lattice relaxation in solid solutions

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Abstract · A Green's function technique is developed for the estimation of lattice relaxation in alkali halide and metallic solid solutions For a finite concentration of defects, we do not consider the defect-defect interaction directly, but assume the crystal to be an elastic continuum where distortions due to different defect ions get superposed in such a way that at any stage of the process the defect crystal retains its perfect lattice structure with a modified lattice parameter. We use Huang's idea of uniform lattice dilatation to determine $r(\chi)$, nearest neighbour (n n) separation as a function of concentration (χ) of substitutional impurities over the entire concentration range (χ = 0 to 1) We have estimated the n n relaxations u_1 and u_2 from a static Green's function model. Application of the present model to alkali halide and metallic solid solutions shows encouraging results. For alkali halide (KCl-KBr and NaCl-KCl) solid solutions, we consider repulsive two-body Born-Meyer type interaction and for metallic (Cu-Au and Cu-Ni) solid solutions, we take Morse potential function to determine the n.n. relaxations

Keywords · Vegard's laws, Lattice relaxation, Green's function

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1. Introduction

From early works on equilibrium diagram, it is clear that the first addition of one binary compound to another binary compound does not produce a new phase, but leads to a homogeneous alloy which is regarded as a solid solution of one binary compound in the other. X-ray diffraction photographs show that the general pattern of the lines or spots remain the same both for the solid solvent and for the solid solutions but the exact position of the lines or spots differ slightly for the two cases. These investigations indicate that the solid solution has the same structure as the parent crystal and formation of substitutional solid solution is accompanied with a uniform lattice relaxation, either contraction or expansion.

In the present work, we have extended the Green's function technique developed by us [1] to find the virtual crystal nearest neighbour (n. n.) separation $r(\chi)$ in terms of the n.n. ion pair separation $r_{A\leftrightarrow X}$ and $r_{B\leftrightarrow X}$ corresponding to some defect concentration χ. It is interesting to note that Vegard's [2] law suggests a linear dependence of χ for $r(\chi)$, whereas the present model finds a quadratic dependence of $r(\chi)$ on χ along with a linear dependence, which seems to be quite significant from the non-linear nature of the experimental curves, for all available alkali halide and metallic solid solutions. We have plotted deviation from the Vegard's law, $[r(\chi) - r_v]$, where r_v (it is defined in eq. (10)) is the n.n. separation according to Vegard's law, from the present model and compared with experimental values for two alkali halide (KCl-KBr, NaCl-KCl) and two metallic (Cu-Au, Cu-Ni) solid solutions. For each case deviation is in the right direction and the agreement is also fairly encouraging considering the simplicity of the model. Easy handling opportunity makes the model suitable for solid solutions having complicated structures. The model is already tested for dilute metallic solid solutions [3] for which we have got good agreement with the experimental results.

2. Theory

In studies of point defects, it is usual to divide the crystal into two regions. Region I consists of the immediate neighbourhood of the point defect, and this region is treated in details, atomistically. The remaining portion of the crystal is the region II. Using the continuum approximation for the region II, one puts the relaxation of an ion at a distance r from the defect as K/r^2, where K is a constant which we call the defect strength constant. Relaxation of an atom in the region I is denoted by u.

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These u and K are very important in determining the variation of n.n. separation of an alloy with the concentration of substitutional impurities.

In a solid solution AX-BX, at any stage of composition $A_{1-\chi}B_{\chi}X$, if any experiment (e.g. X-ray diffraction experiments) fails to measure the individual relaxations at different sites but yields a relaxation picture on the average, then for this average lattice or virtual lattice, we propose a lattice parameter $r(\chi)$ (n.n. separation) given by

$$r(\chi) = \chi\, r_{B\leftrightarrow X}(\chi) + (1-\chi)\, r_{A\leftrightarrow X}(1-\chi), \tag{1}$$

where $r_{B\leftrightarrow X}(\chi)$ and $r_{A\leftrightarrow X}(1-\chi)$ are the nearest neighbour separations between the ion pairs $B\leftrightarrow X$ and $A\leftrightarrow X$ respectively, measured (EXAF measurements) at the same composition stage. For a finite concentration χ, we consider the concentration to be achieved by successive addition of a single defect. As a result, $r_{A\leftrightarrow X}$ and $r_{B\leftrightarrow X}$ will be changing continually, gradually reaching $r_{A\leftrightarrow X}(1-\chi)$ and $r_{B\leftrightarrow X}(\chi)$ respectively. If in an AX host crystal, a guest ion B replaces an isovalent ion A, then due to this replacement, the X ion which is nearest neighbour to the defect ion B, relaxes by u_1 (say) and as a result n.n. separation $r_{B\leftrightarrow X}(\chi)$ gets relaxed. Following Huang's [4] idea of uniform dilation, we apply dilute concentration relaxation u_1 to find $r_{B\leftrightarrow X}(\chi)$, and obtain

$$r_{B\leftrightarrow X}(\chi) = r_1\left(1 + \frac{4\pi K_1 r_1 \chi}{3v_1}\right) + u_1 \tag{2}$$

where r_1, v_1 are the n.n. separation and atomic volume, respectively, of the perfect AX crystal, χ the mole fraction of defect ion B and K_1 the defect strength constant. Similarly starting from a perfect BX crystal and replacing $\chi'[=(1-\chi)]$ mole fraction of B-ion by isovalent defect ion A, we obtain

$$r_{A\leftrightarrow X}(\chi') = r_2\left(1 + \frac{4\pi K_2 r_2 \chi'}{3v_2}\right) + u_2\,, \tag{3}$$

where u_2 is the dilute concentration relaxation of X ion which is nearest neighbour to defect ion A, r_2 and v_2 are the n.n. separation and atomic volume, respectively, of the perfect BX crystal and K_2 is the defect strength constant.

For estimation of defect strength constant, we refer to our work [1] where a smooth merging of the microscopic relaxation experienced by the near neighbourhood of the defect ion, to the macroscopic strain developed in the further region of the crystal, yields

$$K_1 = k_1\, u_1\, r_1^2 \tag{4}$$

and

$$K_2 = k_2\, u_2\, r_2^2 \tag{5}$$

where k_1 and k_2 are constants to be determined from the boundary conditions. Using the boundary conditions :

(I) at $\chi = 1$,

$r_{B\leftrightarrow X}(\chi) = r_2$ and we get

$$k_1 = \frac{1.5}{\pi}\left(-1 + \frac{r_2 - r_1}{u_1}\right) \tag{6}$$

and

(II) at $\chi' = 1$, $r_{A\leftrightarrow X}(\chi') = r_1$ and we get

$$k_2 = \frac{1.5}{\pi}\left(-1 + \frac{r_1}{u_2}\right) \tag{7}$$

Using eqs. (4-7) in eqs. (2) and (3) respectively, we get

$$r_{B\leftrightarrow X}(\chi) = r_1 + (1-\chi)\, u_1 \tag{8}$$

and

$$r_{A\leftrightarrow X}(\chi') = r_v + (1-\chi')\, u_2 = r_v + \chi u_2\,, \tag{9}$$

where r_v, the n.n. separation according to the Vegard's law [2], given by (writing r_2 for $r_{B\leftrightarrow X}(\chi)$ and r_1 for $r_{A\leftrightarrow X}(\chi')$)

$$r_v = (1-\chi) r_1 + \chi r_2. \tag{10}$$

Substituting (8) and (9) in eq. (1) we obtain the present expression for $r(\chi)$ as

$$r(\chi) = r_1 + \chi(1-\chi)(u_1 + u_2). \tag{11}$$

We have estimated u_1 and u_2 from a static Green's function model discussed in our previous papers [1, 3]. Calculated values of u_1 and u_2 are shown in Table 1. Eq. (11) gives us the virtual lattice parameter as expected in the X-ray diffraction measurements. The method of determination of the Morse potential parameters is discussed in detail in our previous paper [3]. The parameters used in the present paper are taken from [3].

Table 1. Calculated values of relaxations of ions at nearest neighbour sites of the defect ion for dilute defect concentration. The relaxation is given in units of 10^{-8} cm.

System	Relaxation (10^{-8} cm)
Br in KCl	0.084
Cl in KBr	− 0.073
K^+ in NaCl	0.202
Na^+ in KCl	−0.110
Au in Cu	0.0700
Cu in Au	− 0.0262
Ni in Cu	− 0.0062
Cu in Ni	0.0053

3. Results and discussion

In the present work, we have calculated $r(\chi)$, the virtual crystal n.n. separation from eq. (11) utilising $r_{A\leftrightarrow X}$ and $r_{B\leftrightarrow X}$ values

obtained from eq. (8) and (9) respectively. We have presented plots of $\Delta r = [r(\chi) - r_v]$, the deviation from the Vegard's law, over entire composition range for two alkali halide (NaCl-KCl and KCl-KBr in Figures 1 and 2 respectively) and two metallic

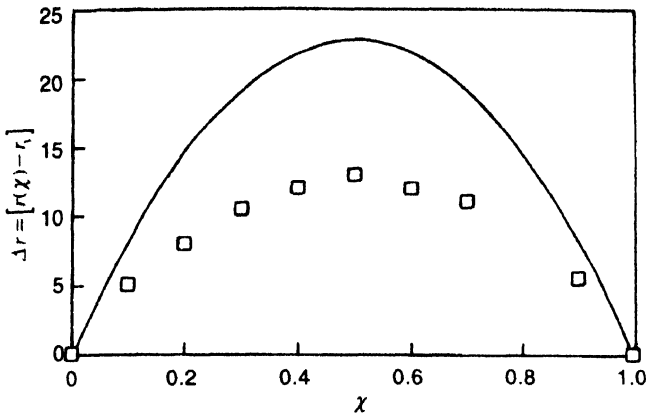

Figure 1. The abscissa of the figure is χ and the ordinate is Δr in 10^{-4} Angström. Comparison of $\Delta r = [r(\chi) - r_v]$, of the deviation of the theoretically calculated values of n n separation $r(\chi)$, from the value suggested by Vegard's law, over the entire composition range to the experimentally observed values for $Na_{(1-\chi)}K_\chi Cl$ alloy Continuous curves are due to the present calculation Experimental values shown by squares, are due to Ahtee [5]

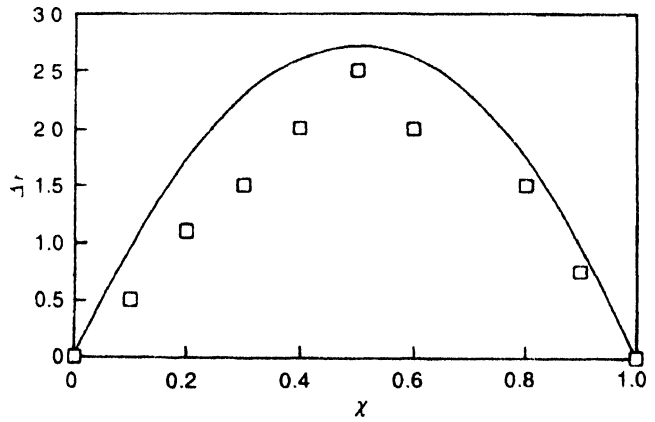

Figure 2. The same as in Figure 1 for $KCl_{(1-\chi)}Br_\chi$ alloy

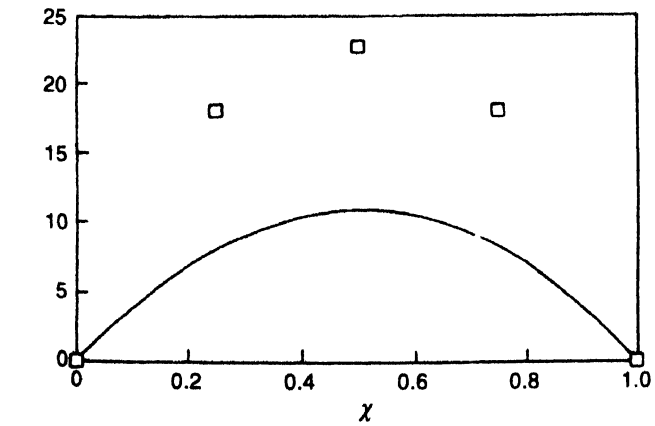

Figure 3. The same as in Figure 1 for $Cu_{(1-\chi)}Au_\chi$ alloy. Experimental (squares) values are due to [6].

solid solution systems (Cu-Au and Cu-Ni in Figures 3, 4) and compared with the corresponding experimental values Considering the uncertainties in measurements as also in input data, the agreement seems to be good (except Cu-Ni solid solution). For Cu-Ni system though the present model predicts the sign of Δr correctly, the quantitative agreement with experiment is very bad. It is significant to note that, all available measurements on alkali halide solid solutions show that the dependence of $r(\chi)$ on χ is not linear in nature as suggested by Vegard's law. The present model correctly obtains the variation of $r(\chi)$ with χ to be of quadratic nature. This model also predicts the sign of the deviation Δr correctly. In case of alkali halides, all available measurements show Δr to be positive as obtained in the present derivation It is significant that the present model also predicts that the sign of Δr is negative for Cu-Ni system. Another interesting point may be mentioned in connection with the Cu-Ni system. Here Δr *vs* χ curve is asymmetrical, as Δr is maximum for $\chi = 0.4$. This asymmetric behaviour can not be explained by the present model, because it is based on the harmonic approximation. The fact that whether (or not) the above asymmetric nature can be reproduced by including anharmonic approximation requires further investigation. Finally, we like to conclude that the present model is quite simple but seems to be fairly useful, particularly, its possible utility in case of two-phase solid solutions with heterostructure solutes, approximated as isotropic solid, makes it worth pursuing.

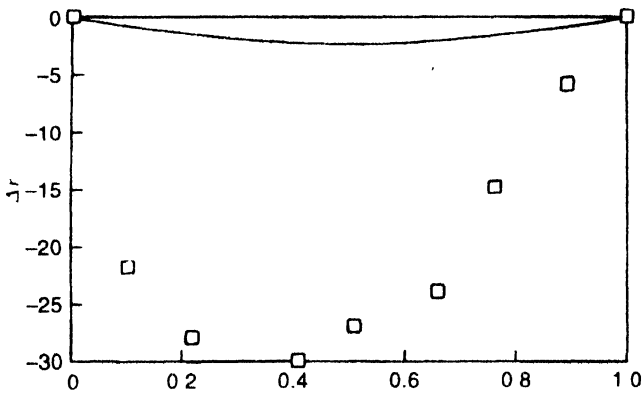

Figure 4. The same as in Figure 1 for $Cu_{(1-\chi)}Ni_\chi$ alloy, but with Δr in 10^{-4} Angström Experimental (squares) values are due to [7]

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